



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ :		(11) International Publication Number:	WO 00/00576
C10M 141/12, 159/12 // (C10M 141/12, 133:56, 133:56), C10N 30:12, 40:25, 60:14	A1	(43) International Publication Date:	6 January 2000 (06.01.00)

(21) International Application Number:	PCT/US99/06204	(81) Designated States:	AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
(22) International Filing Date:	22 March 1999 (22.03.99)		
(30) Priority Data:	09/107,703 ✓ 30 June 1998 (30.06.98)	US	
(71) Applicant:	CHEVRON CHEMICAL COMPANY LLC [US/US]; 555 Market Street, San Francisco, CA 94105 (US).		
(72) Inventors:	HO, Andrew, W.; 2751 Goularte Drive, Pinole, CA 94564 (US). LOGAN, Mark, R.; 59 Arenas Court, San Ramon, CA 94583 (US). WHALEY, Laura, J.; 531 Locust Drive, Vallejo, CA 94591 (US).		
(74) Agents:	LEE, Steven, G., K. et al.; Chevron Corporation, Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).		

(54) Title: ASHLESS LUBRICATING OIL FORMULATIONS FOR NATURAL GAS ENGINES

(57) Abstract

The present invention provides an ashless lubricating oil composition that improves the corrosion properties in natural gas engines. The ashless lubricating oil composition comprises: a) a major amount of base oil of lubricating viscosity; b) from about 1 to 6 wt.% of an untreated polyalkylene or polyalkenyl succinimide dispersant; and c) from about 1 to 6 wt.% of a borated polyalkylene or polyalkenyl succinimide dispersant.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		

ASHLESS LUBRICATING OIL FORMULATIONS FOR NATURAL GAS ENGINES

The present invention relates to an ashless lubricating oil composition. More particularly, the present invention relates to an ashless lubricating oil composition comprising an untreated and a borated polyalkylene or polyalkenyl succinimide dispersant. In a further aspect, this invention relates to a method of preparing this composition and its use in natural gas engine oils. The composition of this invention provides improved corrosion protection in natural gas engines.

BACKGROUND OF THE INVENTION

One of the causes of wear in an internal combustion engine is corrosion of the metal surfaces of the engine, particularly lead and copper metal surfaces caused by the action of various corrosion-promoting compounds which accumulate in the crankcase of the engine. The corrosion-promoting compounds present in the crankcase are principally weak organic acids which may result from nitration and oxidation of the lubricating oil due to contamination by blow-by gases and exposure of the lubricant to high temperatures in the piston and ring zones. Regardless of the source of the corrosion-promoting compounds, it is important to protect the engine from the deleterious action of such compounds and thereby reduce engine wear. For the purpose of preventing corrosivity by these compounds on the various engine parts, it is necessary to incorporate dispersants, detergents, and corrosion inhibitors in the lubricating oil composition, to limit the formation of corrosion products and protecting metal surfaces.

Historically, crankcase oils usually contain ash from detergents, anti-wear products with metals, e.g., Zn, Ca, and the like. Although these metal-containing organic compounds have corrosion inhibition activity as well as detergency, they form undesirable ash deposits in the engine. Ash deposits can lower engine performance by fouling spark plugs, contributing to combustion chamber deposits that cause preignition, or facilitating carbon deposits in two-cycle engine ports and thus are undesirable in many applications. However, it is quite challenging to control corrosion without metal-containing additives like detergents and anti-wear agents. Ashless lubricants would have the advantage of reducing combustion chamber deposits. For example, U.S. Patent No. 5,320,765, issued on June 14, 1994 to Fetterman, Jr. et al.,

disclose marked reductions in diesel engine carbon deposits with lubricating oil compositions containing a high molecular weight ashless dispersant, oil soluble antioxidants, and oil soluble dihydrocarbyl dithiophosphate.

Currently, ashless products are created with metal pacifiers such as terephthalic acid (TPA) to protect the metal surface. However, as highly effective as TPA is in corrosion inhibition, it is very oil insoluble and may contribute to deposits in the engine at low engine temperatures. Thus, it would be desirable to attain the corrosion inhibition performance comparable to TPA but devoid of the insoluble deposit problem associated with TPA.

10 It is also desirable to minimize the amount of phosphorus in lubricants. Although phosphorus does not contribute to ash, it can lead to poisoning of catalysts in pollution control devices such as emission catalysts or traps when amounts of phosphorus make their way into the exhaust system. Exemplary of references directed to the reduction in phosphorus-containing lubricant additives are U.S. Patents Nos. 15 4,147,640, 4,330,420, and 4,639,324.

20 Combined dispersant-corrosion inhibitors are known in the art. For instance, U.S. Patent No. 3,287,271, issued November 22, 1966 to Stuart, discloses a novel composition which provides both corrosion inhibition and detergency by combining a polyamine with a high molecular weight succinic anhydride and then contacting the resulting product with a dicarboxylic acid, having the carboxyl groups separated by at least three annular carbon atoms.

25 U.S. Patent Application No. 09/015,801, filed January 29, 1998, discloses a lubricating oil composition for internal combustion engines giving improved soot dispersancy. That lubricating oil composition has a mixture of borated and carbonated polyalkylene succinimides derived from different molecular weight polyalkylenes. The molecular weight of the polyalkylenes from which the carbonated polyalkylene succinimide is derived is at least 300 greater than the molecular weight of the polyalkylenes from which the borated polyalkylene succinimide is derived. The lubricating oil compositions of the examples contained in this application included 30 significant portions of metal detergents and zinc dithiophosphates creating high ash content and high phosphorus content formulation.

SUMMARY OF THE INVENTION

Pursuant to this invention, an ashless lubricating oil composition suitable for natural gas engines, which provides adequate corrosion inhibition yet contains little or no metal-containing additives, is provided. This invention is obtained by including a 5 borated succinimide dispersant in the formulation. As demonstrated by the CRC L-38 test, which is an industry standard test for corrosiveness, the inclusion of a borated succinimide dispersant in an ashless formulation provides for surprising improved corrosion performance. The ashless lubricating oil composition of the present invention also has a low phosphorus, low ash content. Moreover, the insoluble deposit problem 10 associated with TPA can also be avoided.

The present invention provides an ashless lubricating oil composition comprising:

- a) a major amount of base oil of lubricating viscosity;
- b) from about 1 to 6 wt % of a untreated polyalkylene or polyalkenyl 15 succinimide dispersant; and
- c) from about 1 to 6 wt % of a borated polyalkylene or polyalkenyl succinimide dispersant.

The untreated and borated polyalkylene or polyalkenyl succinimide dispersants are independently derived from a hydrocarbyl group having an average molecular 20 weight of about 600 to 3,000; more preferably from about 950 to 2,500; most preferably about 1,300. Preferably, the polyalkylene or polyalkenyl group is a hydrocarbyl group derived from polypropylene, polybutene, or polyalphaolefin oligomers of 1-octene or 1-decene. Most preferably, the polyalkylene or polyalkenyl group is a hydrocarbyl group derived from polyisobutene. Still more preferably, the polyisobutene contains at least 25 about 20 wt % of a methylvinylidene isomer.

The untreated polyalkylene or polyalkenyl succinimide dispersant can be prepared by reacting under reactive conditions, a mixture of a polybutene succinic acid derivative, an unsaturated acidic reagent copolymer of an unsaturated acidic reagent and an olefin, and a polyamine. Likewise, the borated polyalkylene or polyalkenyl 30 succinimide dispersant can be similarly prepared followed by further treatment with a boron compound.

The present invention further provides a method of producing the ashless lubricating oil composition by blending a mixture of a major amount of a base oil of lubricating viscosity and an effective amount of an untreated and borated polyalkylene or polyalkenyl succinimide dispersant of the present invention.

5 Among other factors, the present invention is based on the surprising discovery that the corrosion properties in a natural gas engine can be improved by adding an effective amount of a lubricating oil composition of the present invention. More particularly, the present invention relates to an ashless lubricating oil composition comprising an untreated and a borated polyalkylene or polyalkenyl succinimide dispersant. Formulations containing the untreated succinimide dispersant without the borated succinimide dispersant failed to demonstrate any improvement in corrosion performance. Using the borated succinimide exclusively would require too high a concentration of borated material which would exceed the ash limitation considered to be ashless. It is important that the ash content remain below 0.10 wt % for the purpose 10 of this invention.

15

DETAILED DESCRIPTION OF THE INVENTION

As mentioned above, the present invention provides an ashless lubricating oil composition that improves the corrosion properties in natural gas engines. Prior to discussing the present invention in further detail, the following terms will be defined.

20 Definitions

As used herein the following terms have the following meanings unless expressly stated to the contrary.

25 The term "ash" refers to a metal-containing compound wherein the metal can be zinc, sodium, potassium, magnesium, calcium, lithium, barium, and the like, as measured by ASTM D874.

The term "ashless" refers to less than 0.10 wt % ash content in the lubricating oil composition.

30 The term "hydrocarbyl" refers to an organic radical primarily composed of carbon and hydrogen which may be aliphatic, alicyclic, aromatic or combinations thereof, e.g., aralkyl or alkaryl. Such hydrocarbyl groups are generally free of aliphatic unsaturation, i.e., olefinic or acetylenic unsaturation, but may contain minor amounts of heteroatoms, such as oxygen or nitrogen, or halogens, such as chlorine.

The term "succinimide" is understood in the art to include many of the amide, imide, etc. species which are also formed by the reaction of a succinic anhydride with an amine and is so used herein. The predominant product, however, is succinimide and this term has been generally accepted as meaning the product of a reaction of an 5 alkenyl- or alkyl-substituted succinic acid or anhydride with a polyamine. Alkenyl or alkyl succinimides are disclosed in numerous references and are well known in the art. Certain fundamental types of succinimides and related materials encompassed by the term of art "succinimide" are taught in U.S. Patent Nos. 2,992,708; 3,018,250; 3,018,291; 3,024,237; 3,100,673; 3,172,892; 3,219,666; 3,272,746; 3,361,673; 10 3,381,022; 3,912,764; 4,234,435; 4,612,132; 4,747,965; 5,112,507; 5,241,003; 5,266,186; 5,286,799; 5,319,030; 5,334,321; 5,356,552; 5,716,912, the disclosures of which are hereby incorporated by reference.

The term "untreated" refers to a polyalkylene or alkenyl succinimide which has not been further treated with a cyclic carbonate or linear mono- or poly-carbonate or 15 boron oxide, boron halide, boric acid, and esters of boric acid, under reactive conditions.

The term "base oil of lubricating viscosity" generally refers to an oil having a viscosity of 3-20 cSt at 100°C in the case of lubricating oil compositions and may be a single oil or a blend of oils.

20

SUCCINIMIDE DISPERSANT

The present invention relates to an ashless lubricating oil composition involving a combination of untreated and borated succinimide dispersants.

Untreated Succinimide Dispersant

25 Preferably, the lubricating oil composition of the present invention comprises from about 1 to 6 wt % of a untreated polyalkylene or polyalkenyl succinimide dispersant.

The polyalkylene or polyalkenyl succinimide dispersants used in the lubricating oil composition of the present invention can be prepared by conventional processes. In brief, the untreated, borated succinimide dispersant is preferably prepared by reacting 30 under reactive conditions a mixture of a polybutene succinic acid derivative, an unsaturated acidic reagent copolymer of an unsaturated acidic reagent and an olefin, and a polyamine, such as disclosed in U.S. Patent No. 2,992,708; 3,018,250; 3,018,291;

3,024,237; 3,100,673; 3,172,892; 3,219,666; 3,272,746; 3,361,673; 3,381,022; 3,912,764; 4,234,435; 4,612,132; 4,747,965; 5,112,507; 5,241,003; 5,266,186; 5,286,799; 5,319,030; 5,334,321; 5,356,552; 5,716,912, the disclosures of which are all hereby incorporated by reference in their entirety for all purposes.

5 More than one untreated polyalkylene or polyalkenyl succinimide dispersant may be present in the lubricating oil composition. Additionally, the lubricating oil composition may also contain a non-borated polyalkylene or polyalkenyl succinimide dispersant that has been post-treated with ethylene carbonate. However, as exemplified in the example below, the addition of a non-borated polyalkylene or polyalkenyl succinimide dispersant that has been post-treated with ethylene carbonate does not necessarily improve the overall wear performance of the lubricating oil formulation.

10

Borated Succinimide Dispersant

15 Preferably, the lubricating oil composition of the present invention comprises from about 1 to 6 wt % of a borated polyalkylene or polyalkenyl succinimide dispersant.

The borated succinimide dispersant is preferably prepared by reacting under reactive conditions a mixture of a polybutene succinic acid derivative, an unsaturated acidic reagent copolymer of an unsaturated acidic reagent and an olefin, and a polyamine, such as taught in U.S. Patent No. 5,716,912, to prepare the succinimide, 20 followed by treatment with a boron compound selected from the group consisting of boron oxide, boron halide, boric acid, and esters of boric acid, under reactive conditions. Similarly by following the similar procedure, the untreated succinimide described above can be borated. The borated succinimide dispersant is from about 1 to 6 wt % of the lubricating oil composition.

25 The advantages of the borated polyalkylene or polyalkenyl succinimide dispersant are TBN contribution and prevention of corrosion. Without the borated succinimide dispersant in the low ash lubricating formulation, as shown in the comparatives examples described below, bearing weight loss increased significantly, an indication that increased wear occurred. Hence, it is the addition of the borated 30 succinimide dispersant to the untreated succinimide that provides the unexpected anti-wear performance.

The present lubricating oil composition can be prepared by physically mixing the untreated polyalkylene or polyalkenyl succinimide dispersant and the borated polyalkylene or polyalkenyl succinimide dispersant. The polyalkylene or polyalkenyl succinimide composition might have a slightly different composition than the initial mixture, because the components may interact either with each other or other additives to form different compounds or complexes.

BASE OIL OF LUBRICATING VISCOSITY

The base oil of lubricating viscosity used in such compositions may be mineral oils or synthetic oils of viscosity suitable for use in the crankcase of an internal combustion engine. The base oils may be derived from synthetic or natural sources. Mineral oils for use as the base oil in this invention include, for example, paraffinic, naphthenic and other oils that are ordinarily used in lubricating oil compositions. Synthetic oils include, for example, both hydrocarbon synthetic oils and synthetic esters and mixtures thereof having desired viscosity. Useful synthetic hydrocarbon oils include liquid polymers of alpha olefins having the proper viscosity. Especially useful are the hydrogenated liquid oligomers of C₆ to C₁₂ alpha olefins such as 1-decene trimer. Likewise, alkyl benzenes of proper viscosity, such as didodecyl benzene, can be used. Useful synthetic esters include the esters of monocarboxylic acids and polycarboxylic acids, as well as mono-hydroxy alkanols and polyols. Typical examples are didodecyl adipate, pentaerythritol tetracaproate, di-2-ethylhexyl adipate, dilaurylsebacate, and the like. Complex esters prepared from mixtures of mono and dicarboxylic acids and mono and dihydroxy alkanols can also be used. Blends of mineral oils with synthetic oils are also useful.

OTHER ADDITIVE COMPONENTS

The following additive components are examples of some of the components that can be favorably employed in the present invention. These examples of additives are provided to illustrate the present invention, but they are not intended to limit it:

1. **Metal detergents:** sulfurized or unsulfurized alkyl or alkenyl phenates, alkyl or alkenyl aromatic sulfonates, sulfurized or unsulfurized metal salts of multi-hydroxy alkyl or alkenyl aromatic compounds, alkyl or alkenyl hydroxy aromatic sulfonates, sulfurized or unsulfurized alkyl or alkenyl naphthenates,

metal salts of alkanoic acids, metal salts of an alkyl or alkenyl multiacid, and chemical and physical mixtures thereof.

2. **Anti-oxidants:** Anti-oxidants reduce the tendency of mineral oils to deteriorate in service which deterioration is evidenced by the products of oxidation such as 5 sludge and varnish-like deposits on the metal surfaces and by an increase in viscosity. Examples of anti-oxidants useful in the present invention include, but are not limited to, phenol type (phenolic) oxidation inhibitors, such as 4,4'-methylene-bis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-tert-butylphenol), 4,4'-butyldene-bis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidene-bis(2,6-di-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-nonylphenol), 2,2'-isobutylidene-bis(4,6-dimethylphenol), 2,2'-methylene-bis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butyl-phenol, 2,6-di-tert-1-dimethylamino-p-cresol, 2,6-di-tert-4-(N,N'-dimethylaminomethylphenol), 4,4'-thiobis(2-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), bis(3-methyl-4-hydroxy-5-tert-butylbenzyl)-sulfide, and bis(3,5-di-tert-butyl-4-hydroxybenzyl). Diphenylamine-type oxidation inhibitors include, but are not limited to, alkylated diphenylamine, phenyl- α -naphthylamine, and alkylated- α -naphthylamine. Other types of oxidation inhibitors include metal 10 dithiocarbamate (e.g., zinc dithiocarbamate), and methylenebis(dibutylthiocarbamate). The anti-oxidant is generally incorporated into an engine oil in an amount of about 0 to 10 wt %, preferably 15 0.05 to 3.0 wt %, per total amount of the engine oil.

20 3. **Anti-wear agents:** As their name implies, these agents reduce wear of moving metallic parts. Examples of such agents include, but are not limited to, phosphates, phosphites, carbamates, esters, sulfur containing compounds, and molybdenum complexes.

25 4. **Rust inhibitors (Anti-rust agents)**

30 a) **Nonionic polyoxyethylene surface active agents:** polyoxyethylene lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonyl phenyl ether, polyoxyethylene octyl phenyl ether, polyoxyethylene octyl stearyl ether,

polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol mono-oleate, and polyethylene glycol mono-oleate.

5 **b) Other compounds:** stearic acid and other fatty acids, dicarboxylic acids, metal soaps, fatty acid amine salts, metal salts of heavy sulfonic acid, partial carboxylic acid ester of polyhydric alcohol, and phosphoric ester.

5 **5. Demulsifiers:** addition product of alkylphenol and ethylene oxide, polyoxyethylene alkyl ether, and polyoxyethylene sorbitan ester.

10 **6. Extreme pressure agents (EP agents):** zinc dialkyldithiophosphate (primary alkyl, secondary alkyl, and aryl type), sulfurized oils, diphenyl sulfide, methyl trichlorostearate, chlorinated naphthalene, fluoroalkylpolysiloxane, and lead naphthenate.

15 **7. Friction modifiers:** fatty alcohol, fatty acid, amine, borated ester, and other esters.

15 **8. Multifunctional additives:** sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum organo phosphorodithioate, oxymolybdenum monoglyceride, oxymolybdenum diethylate amide, amine-molybdenum complex compound, and sulfur-containing molybdenum complex compound.

20 **9. Viscosity index improvers:** polymethacrylate type polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, hydrated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.

20 **10. Pour point depressants:** polymethyl methacrylate.

20 **11. Foam inhibitors:** alkyl methacrylate polymers and dimethyl silicone polymers.

LUBRICATING OIL COMPOSITION

25 The lubricating oil composition of the present invention is useful for imparting improved corrosion properties to natural gas engines. The lubricating oil composition comprises a major part of base oil of lubricating viscosity and an effective amount of the untreated and borated polyalkylene or polyalkenyl succinimide dispersants. The ash content of the lubricating oil composition of the present invention is less than about 0.10 wt %.

30 In one embodiment, the lubricating oil composition contains:

30 a) a major amount of base oil of lubricating viscosity;

- b) from about 1 to 6 wt % of an untreated polyalkylene or polyalkenyl succinimide dispersant; and
- c) from about 1 to 6 wt % of a borated polyalkylene or polyalkenyl succinimide dispersant.

5 In a further embodiment, a lubricating oil composition is produced by blending a mixture of the above components. The lubricating oil composition produced by that method might have a slightly different composition than the initial mixture, because the components may interact.

10 The components can be blended in any order and can be blended as combinations of components. For example, the untreated polyalkylene or polyalkenyl succinimide dispersant can be blended with the other components before, during, and/or after the boron-treated polyalkylene or polyalkenyl succinimide dispersant, are blended together.

EXAMPLES

15 The following examples are presented to illustrate specific embodiments of the present invention and synthetic preparations thereof; and therefore these examples should not be interpreted as limitations upon the scope of this invention.

EXAMPLE 1: UNTREATED AND BORATED SUCCINIMIDE FORMULATION

The first formulation consists of:

20 a) 2.5 wt % of an untreated succinimide dispersant derived from 1,300 molecular weight polybutene formed by reacting a polybutene-substituted succinic acid with a heavy polyamine,

b) 2.0 wt % of a borated succinimide dispersant derived from 1,300 molecular weight polybutene formed by reacting a polybutene-substituted succinic acid with a heavy polyamine, then post-treating the resulting polybutene succinimide with boric acid,

25 c) 1.0 wt % of an anti-oxidant,

d) 0.16 wt % of an anti-wear inhibitor,

e) 0.003 wt % of a foam inhibitor, and

30 blended with a base oil of lubricating viscosity. Ash content was 0.05 wt %.

EXAMPLE 2: UNTREATED AND BORATED SUCCINIMIDE FORMULATION

The second formulation consists of :

- a) 2.5 wt % of an untreated succinimide dispersant derived from 1,300 molecular weight polybutene formed by reacting a polybutene-substituted succinic acid with a heavy polyamine,
- 5 b) 2.0 wt % a borated succinimide dispersant derived from 1,300 molecular weight polybutene formed by reacting a polybutene-substituted succinic acid with a heavy polyamine, then post-treating the resulting polybutene succinimide with boric acid,
- c) 1.5 wt % of an anti-oxidant,
- 10 d) 0.08 wt % of an anti-wear inhibitor,
- e) 0.003 wt % of a foam inhibitor, and

blended with a base oil of lubricating viscosity. Ash content was 0.02 wt %.

EXAMPLE 3: UNTREATED AND BORATED SUCCINIMIDE

FORMULATION

15 Example 3 demonstrates that this invention also works when multiple non-borated succinimides are used. This example illustrates a situation where one untreated succinimide is not post-treated with ethylene carbonated and the other non-borated succinimide is ethylene carbonate post-treated. The third formulation consists of:

- a) 2.25 wt % of an untreated succinimide dispersant derived from 1,300 molecular weight polybutene formed by reacting a polybutene-substituted succinic acid with a heavy polyamine,
- 20 b) 2.25 wt % of a non-borated succinimide dispersant derived from 2,200 molecular weight polybutene formed by reacting a polybutene-substituted succinic acid with a heavy polyamine that is subsequently post-treated with ethylene carbonate,
- c) 2.0 wt % of a borated succinimide dispersant derived from 1,300 molecular weight polybutene formed by reacting a polybutene-substituted succinic acid with a heavy polyamine, then post-treating the resulting polybutene succinimide with boric acid,
- 25 d) 2.53 wt % of anti-oxidants,
- e) 0.02 wt % of an anti-wear inhibitor,
- 30 f) 0.10 wt % of a detergent, and

blended with a base oil of lubricating viscosity. Ash content was 0.04 wt %.

COMPARATIVE EXAMPLE A: UNTREATED SUCCINIMIDE FORMULATION

The fourth formulation consists of:

5 a) 4.5 wt % of an untreated succinimide dispersant derived from 1,300 molecular weight polybutene formed by reacting a polybutene-substituted succinic acid with a heavy polyamine,

 b) 1.0 wt % of an anti-oxidant,

 c) 0.16 wt % of an anti-wear inhibitor,

10 d) 0.003 wt % of a foam inhibitor, and

blended with a base oil of lubricating viscosity. Ash content was 0.01 wt %.

COMPARATIVE EXAMPLE B: UNTREATED SUCCINIMIDE FORMULATION

The fifth formulation consists of:

15 a) 2.25 wt % of an untreated succinimide dispersant derived from 1,300 molecular weight polybutene formed by reacting a polybutene-substituted succinic acid with a heavy polyamine.

 b) 2.25 wt % of a non-borated succinimide dispersant derived from 2,200 molecular weight polybutene formed by reacting a polybutene-substituted succinic acid with a heavy polyamine that is subsequently post-treated with ethylene carbonate.

20 c) 2.53 wt % of anti-oxidants,

 d) 0.02 wt % of an anti-wear inhibitor,

 e) 0.10 wt % of a detergent, and

25 blended with a base oil of lubricating viscosity. Ash content was 0.01 wt %.

TEST RESULTS OF EXAMPLES 1-3 AND COMPARATIVE EXAMPLES A-B

The bearing weight loss of a lubricating oil formulation containing an effective amount of both the untreated and borated polyalkylene or polyalkenyl succinimide dispersants (Example 1 and 2) of the present invention were compared to the bearing weight loss of a lubricating oil formulation having only the untreated polyalkylene or polyalkenyl succinimide (Comparative Example A). Example 3 shows the results of a

run for a formulation with a combination of an untreated succinimide and an ethylene carbonated succinimide with a borated succinimide. Comparative Example B shows the results of a formulation of Example 3 without a borated succinimide. The CRC L-38 test is a standard industry test that measures the corrosiveness of oil in terms of bearing weight loss. Bearing weight loss below 40 mg is considered passing. The lower the number the better the result. The results are shown in the table below.

	EXAMPLES			COMPARATIVE EXAMPLES	
	1	2	3	A	B
Untreated Succinimide, wt %	2.5	2.5	2.25	4.5	2.25
Non-Borated, Ethylene Carbonated Post-treated Succinimide, wt %	-	-	2.25	-	2.25
Borated Succinimide, wt %	2.0	2.0	2.0	-	-
Anti-oxidants, wt %	1.0	1.5	2.53	1.0	2.53
Anti-wear, wt %	0.16	0.08	0.02	0.16	0.02
Detergent, wt %	-	-	0.10	-	0.10
Foam Inhibitor, wt %	0.003	0.003	-	0.003	-
Bearing Weight Loss, mg	28.2	18.4	19.9	71.1	316.6
Results	PASS	PASS	PASS	FAIL	FAIL

The above results show the surprising benefit of the borated succinimide dispersants in passivating L-38 bearing weight loss demonstrating improved corrosion performance. When the borated succinimide dispersants were not incorporated as shown in the comparative examples, the bearing weight loss increased significantly beyond the passing threshold. Hence, it is the addition of the borated succinimide dispersant to the untreated succinimide that provides the unexpected anti-wear performance.

While the present invention has been described with reference to specific embodiments, this application is intended to cover those various changes and substitutions that may be made by those skilled in the art without departing from the spirit and scope of the appended claims.

WHAT IS CLAIMED IS:

1. A lubricating oil composition comprising:
 - a) a major amount of a base oil of lubricating viscosity;
 - b) from about 1 to 6 wt % of an untreated polyalkylene or polyalkenyl succinimide dispersant; and
 - c) from about 1 to 6 wt % of a borated polyalkylene or polyalkenyl succinimide dispersant.
2. A lubricating oil composition according to Claim 1, wherein the ash content of said lubricating oil composition is less than about 0.10 wt %.
- 10 3. A lubricating oil composition according to Claim 1, wherein said lubricating oil composition further comprises from about 0.05 to 3.0 wt % of at least one antioxidant.
4. A lubricating oil composition according to Claim 3, wherein said lubricating oil composition further comprises from about 0.01 to 1.0 wt % of at least one anti-wear agent.
- 15 5. A lubricating oil composition according to Claim 1, wherein the polyalkylene or polyalkenyl group of the untreated succinimide dispersant is a hydrocarbyl group having an average molecular weight of about 600 to 3,000, and the polyalkylene or polyalkenyl group of the borated succinimide dispersant is independently a hydrocarbyl group having an average molecular weight of about 600 to 3,000.
- 20 6. A lubricating oil composition according to Claim 5, wherein the polyalkylene or polyalkenyl group of the untreated succinimide dispersant is a hydrocarbyl group having an average molecular weight of about 950 to 2,500, and the polyalkylene or polyalkenyl group of the borated succinimide dispersant is independently a hydrocarbyl group having an average molecular weight of about 950 to 2,500.
- 25 7. A lubricating oil composition according to Claim 6, wherein the polyalkylene or polyalkenyl group of the untreated succinimide dispersant is a hydrocarbyl group having an average molecular weight of about 1,300, and the polyalkylene or polyalkenyl group of the borated succinimide dispersant is independently a hydrocarbyl group having an average molecular weight of about 1,300.

8. A lubricating oil composition according to Claim 1, wherein the polyalkylene or polyalkenyl group of the untreated succinimide dispersant is a hydrocarbyl group derived from polypropylene, polybutene, or polyalphaolefin oligomers of 1-octene or 1-decene, and the polyalkylene or polyalkenyl group of the borated succinimide dispersant is independently a hydrocarbyl group derived from polypropylene, polybutene, or polyalphaolefin oligomers of 1-octene or 1-decene.
5
9. A lubricating oil composition according to Claim 8, wherein said hydrocarbyl group is derived from polyisobutene.
10. A lubricating oil composition according to Claim 9, wherein the polyisobutene contains at least about 20 wt % of a methylvinylidene isomer.
11. A lubricating oil composition according to Claim 1, wherein the untreated polyalkylene or polyalkenyl succinimide dispersant is prepared by reacting a mixture under reactive conditions, wherein the mixture comprises:
15
 - a) a polybutene succinic acid derivative;
 - b) an unsaturated acidic reagent copolymer of an unsaturated acidic reagent and an olefin; and
 - c) a polyamine.
12. A lubricating oil composition according to Claim 1, wherein the borated polyalkylene or polyalkenyl succinimide dispersant is prepared by reacting a mixture under reactive conditions, wherein the mixture comprises:
20
 - a) a polybutene succinic acid derivative;
 - b) an unsaturated acidic reagent copolymer of an unsaturated acidic reagent and an olefin; and
 - c) a polyamine;
- 25 followed by treatment with a boron compound selected from a group consisting of boron oxide, boron halide, boric acid, and esters of boric acid, under reactive conditions.
13. A method of producing a lubricating oil composition comprising blending the following components together:
30
 - a) a major amount of a base oil of lubricating viscosity;

- b) from about 1 to 6 wt % of an untreated polyalkylene or polyalkenyl succinimide dispersant; and
- c) from about 1 to 6 wt % of a borated polyalkylene or polyalkenyl succinimide dispersant.

5 14. A lubricating oil composition produced by the method according to Claim 13.

15. A method for improving corrosion protection of an internal combustion engine, said method comprising lubricating said engine with a lubricating oil composition according to Claim 1.

16. A method according to Claim 15, wherein the internal combustion engine is a natural gas engine.

10

INTERNATIONAL SEARCH REPORT

Int'l. Application No
PCT/US 99/06204

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C10M141/12 C10M159/12 // (C10M141/12, C10M133:56, C10M133:56),
C10N30:12, 40:25, 60:14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 562 172 A (IDEMITSU KOSAN CO) 29 September 1993	1-14
A	see page 2, line 11 - page 2, line 16 see page 3, line 15 - page 3, line 21 see example 4 see page 7, line 54 see page 7, line 56 ---	15, 16
Y	EP 0 839 840 A (IDEMITSU KOSAN CO) 6 May 1998 see abstract see page 2, line 44 - page 2, line 48 see page 3, line 26 - page 3, line 48 see page 5, line 46 - page 5, line 54 ---	1-16 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority, claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the International search report
7 July 1999	14/07/1999
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Authorized officer Perakis, N

INTERNATIONAL SEARCH REPORT

Inte onal Application No

PCT/US 99/06204

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 554 086 A (KAROL THOMAS J ET AL) 19 November 1985 see abstract see column 1, line 11 - column 1, line 13 see column 1, line 40 - column 1, line 44 see column 2, line 17 - column 3, line 50 see column 7, line 19 - column 8, line 40 ----	1-16
Y	US 5 716 912 A (RUHE JR WILLIAM R ET AL) 10 February 1998 see abstract see column 1, line 4 - column 1, line 22 see column 3, line 51 - column 4, line 34 see column 5, line 14 - column 5, line 49 see column 10, line 22 - column 10, line 44 see column 14, line 22 - column 14, line 29 see column 25, line 24 - column 25, line 33 ----	1-16
A	US 5 726 133 A (BLAHEY ALAN G ET AL) 10 March 1998 see abstract see column 2, line 1 - column 2, line 27 see column 4, line 16 - column 4, line 26 ----	1-16
A	GB 1 368 277 A (SHELL INT RESEARCH) 25 September 1974 see page 1, line 11 - page 1, line 85 see page 2, line 67 - page 2, line 76 see table 1 see page 6, line 35 - page 7, line 3 -----	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/06204

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
EP 0562172	A 29-09-1993	JP 5163497	A	29-06-1993	
		CA 2085074	A	13-06-1993	
		DE 69228677	D	22-04-1999	
		US 5458807	A	17-10-1995	
EP 0839840	A 06-05-1998	JP 11021278	A	26-01-1999	
US 4554086	A 19-11-1985	NONE			
US 5716912	A 10-02-1998	NONE			
US 5726133	A 10-03-1998	CA 2245532	A	04-09-1997	
		EP 0883667	A	16-12-1998	
		WO 9731991	A	04-09-1997	
GB 1368277	A 25-09-1974	AU 466753	B	06-11-1975	
		AU 3510771	A	03-05-1973	
		BE 774297	A	24-04-1972	
		CA 949956	A	25-06-1974	
		DE 2153893	A	04-05-1972	
		FR 2111941	A	09-06-1972	
		NL 7114830	A	03-05-1972	
		SE 381281	B	01-12-1975	